Polymerization of Vegetable Oils and Their Uses in Printing Inks

S.Z. Erhan* and **M.O. Bagby**
NCAUR, ARS, USDA, Peoria, Illinois 61604

Ink vehicles were prepared by the polymerization of vegetable oils. By controlling the polymerization conditions, the desired viscosity, color and molecular weight could be achieved for a variety of vegetable oils with a broad range of iodine values and fatty acid compositions. The effect of temperature and catalyst on polymerization rates were evaluated, and polymerization rate constants were calculated. Of the oils tested, the polymerization rate constant of safflower oil was the highest, followed by soybean, sunflower, cottonseed and canola oils in decreasing order. Use of a catalyst shortened the heating time by about 25–50% or lowered the polymerization temperature requirement by 25–30°C.

KEY WORDS: Polymerization, printing inks, rate constant, vegetable oils, vehicles.

The petroleum shortages in the 1970s stimulated research on identifying alternative and renewable materials for preparation of printing ink vehicles and ink formulations. Because of their well-known characteristics of being nonvolatile and biodegradable, vegetable oils were an obvious choice for further investigation. Inks containing vegetable oils have been formulated for various applications (1–5). In the early 1980s, the American Newspaper Publishers Association (ANPA) developed a series of ink formulations comprising a blend of "gilsonite" and tall oil fatty acids together with carbon black pigment (6–8). Gilsonite is solidified hydrocarbon and has strong pigmenting properties. Acceptance of these inks by the industry has been limited by the cost and availability of tall oil and the difficulty of equipment cleanup caused by the gilsonite.

In 1987, ANPA introduced a vegetable oil-based ink vehicle suitable for lithographic news ink, comprising alkali-refined soybean oil, a hydrocarbon resin and pigments (9). Although the color inks have become commercial, widespread acceptance of black ink has been inhibited by cost. Both the black and color inks contain 20–25% hydrocarbon resin. Thus, the industry has continued to seek vegetable oil-based nonpetroleum ink.

Because of its availability and favorable price, we emphasized soybean oil in our research. However, other vegetable oils were included that allowed evaluation of the influence of their compositions on the preparation and properties of the vehicle. Of special interest were the effects of unsaturation (iodine value, IV) and the presence of various fatty acids found in commodity oils available worldwide. To study oils with a broad IV range which contained saturated, monounsaturated, diunsaturated and triunsaturated acids, we selected alkali-refined canola, cottonseed, soybean, sunflower and safflower oils. Alkali refining removes the gums, waxes and free fatty acids. The presence of any one of these materials will interfere with the desirable hydrophobic characteristics of the vehicle, as well as the ultimate ink formulation.

These hydrophobic characteristics deserve further comment. The offset printer plate or cylinder consists of two distinct areas. One area has been rendered hydrophobic (image area), and the nonimage area is hydrophilic. The offset printing process involves a two-phase system consisting of an oil phase (the ink) and an aqueous phase (the fountain solution). These phases must not form stable emulsions during the printing process, or they will not separate properly on the printing plates. Poorly separated phases lead to smudges or ill-defined print. Understanding of this characteristic directed our attention toward techniques for modifying vegetable oils that would provide relatively nonpolar products, i.e., low-oxygen content polymers. The vehicles were prepared from vegetable oils by two methods. In the first method, vegetable oils were heat-polymerized at a constant temperature in nitrogen atmosphere to a desired viscosity. In the second method, the heat-polymerization reaction was permitted to proceed to a gel point, and then the gel was mixed with vegetable oils to obtain a desired viscosity. In addition, the first method was repeated by using a catalyst to shorten the heating time. Here we discuss the effect of composition of oil, temperature and catalyst on the polymerization rate and rate constants of polymerization at constant and varying temperatures.

EXPERIMENTAL PROCEDURES

Materials. Alkali-refined soybean oil was obtained from Riceland Foods (Stuttgart, AR) and Archer Daniels Midland (Decatur, IL). Alkali-refined canola and cottonseed oils were purchased from Bunge Oil (Bradley, IL). Alkali-refined sunflower oil was obtained from Archer Daniels Midland. Alkali-refined safflower oil was obtained from Pacific Anchor Chemical Co. (Cumberland, RI). Polystyrene standards were obtained from Polymer Laboratories, Ltd. (Amherst, MA), and had the following specifications: (peak average molecular weight and molecular weight distribution) 580, 1.14; 1320, 1.09; 3250, 1.04; 9200, 1.03; 28500, 1.03; 66000, 1.03; 156000, 1.03; 435500, 1.04; 1030000, 1.05; 2250000, 1.04; and 2880000, 1.04.

Methods. Vehicles were prepared in a four-necked reaction flask equipped with a mechanical stirrer. Two major methods were used in preparation of polymers: Method A—alkali-refined vegetable oil was polymerized with stirring at 330 ± 3°C in nitrogen atmosphere to the desired viscosity; some polymers prepared by this method were used directly as vehicles, others with Gardner-Holdt viscosities as high as Z_8–Z_9, were admixed with low-viscosity polymers and/or unmodified, alkali-refined vegetable oil at 67–75°C in a reaction flask equipped with a mechanical stirrer. Method B—heat-bodying was continued until the oil gelled. The reaction was discontinued at the transition point when clumps of gel began to climb up the shaft of the mechanical stirrer. The gel was blended in various ratios with unmodified alkali-refined vegetable oil at 330 ± 3°C. The heating softened the gel and promoted blending. Agitation was continued until a smooth vehicle was obtained. The proportions of the gel and unmodified oil determined the resultant vehicle viscosities.

Method A was repeated at 280, 290, 300, 310 and 320 ± 3°C to determine the effect of temperature on the rate constant. Method A was also repeated at 300 ± 3°C and

*To whom correspondence should be addressed at NCAUR, 1815 N. University, Peoria, IL 61604.

330 ± 3°C with 5% by weight of anthraquinone catalyst. Heating was terminated when the desired viscosity was reached. The heat-bodied oil was allowed to cool to room temperature and then filtered to remove the precipitated catalyst.

The viscosities of all vehicles were determined with a Gardner-Holdt Bubble Viscometer by following the American Society for Testing and Materials Method ASTM D-1545-63 (10). The color of each vehicle was evaluated on the Gardner Color Scale by ASTM D-1544-63 (11).

The IVs were obtained by the American Oil Chemists' Society (AOCS) Cd.I.25 Wijs Method (12), and free fatty acid values were obtained by AOCS Method Ca 5a-40 (12).

For gel permeation chromatography (GPC) analysis, the samples were dissolved in tetrahydrofuran (0.4%, wt/vol), filtered through 0.5-μm Teflon filters, and then injected into the high-performance liquid chromatograph (Model 8100; Spectra Physics, San Jose, CA). Chromatography operating conditions were: flow, 1 mL/min; oven temperature, 40°C; column 30 cm × 7.5 mm, PL-Gel 5-μm mix; detector, differential refractive index (model 6040; Spectra Physics); and injection volume, 50 μL.

RESULTS AND DISCUSSION

The vehicles that we prepared typically had viscosity values in the range of G-Y on the Gardner-Holdt Viscometer Scale or about 1.6–18 poises (13). These viscosities correspond to apparent weight average molecular weights (Mw) that range from 2600–8900 (14). As the oils are heated, they undergo polymerization and isomerization reactions. Thus, Mw's and viscosities increase. The more highly unsaturated oils, containing greater amounts of linoleic and linolenic acids and having the higher IV, of course, react more rapidly (13). As expected, the polymerized oils showed reduced IV (Table 1), and the free fatty acid contents remained low (Table 2). Thus, the desired hydrophobic characteristics of vegetable oils were retained.

Plots of the logarithm of viscosity data against time are linear (Fig. 1). The polymerization rate constants were calculated from the slope of the plot of each oil at a constant temperature:

$$K = \frac{\log V_2 - \log V_1}{t_2 - t_1} \qquad [1]$$

where V_2 and V_1 are the viscosity in centipoises, and t_2 and t_1 are times in minutes. Table 3 shows the K values for each oil.

Figure 2 plots the logarithm of viscosity data against time for soybean oil at different temperatures. Calculated polymerization rate constants from Equation 1 and corresponding temperatures are tabulated in Table 4. Figures 3 and 4 show the logarithm of viscosity against time plot of polymerization data for soybean oil, both with and without catalyst at 300 ± 3°C and 330 ± 3°C. Rate constants with and without catalyst at 300 ± 3°C and 330 ± 3°C were 9.81 × 10^{-3}, 5.73 × 10^{-3} and 15.50 × 10^{-3}, 11.02 × 10^{-3}, respectively. A catalyst shortens the heating time by about 25–50% or can lower the polymerization temperature by 25–30°C.

TABLE 1

Iodine Values of Polymerized Vegetable Oils

	Iodine values				
Oil	Unreacted	V–W[a]	W–X[a]	X–Y[a]	Gel
Safflower	142.3	108.9	104.0	104.5	84.0
Soybean	127.7	51.7	50.9	52.1	79.2
Sunflower	133.4	99.4	103.1	96.8	71.1
Cottonseed	112.4	86.0	83.1	77.0	69.0
Canola	110.2	91.5	91.4	92.0	79.5

[a]V, W, X and Y are Gardner-Holdt viscosities; gel does not flow under prescribed conditions.

TABLE 2

Free Fatty Acids in Polymerized Vegetable Oils

	Free fatty (%)[a]				
Oil	Unreacted	V–W[b]	W–X[b]	X–Y[b]	Gel[b]
Safflower	0.12	0.74	0.61	0.98	2.79
Soybean	0.09	1.24	1.59	2.11	5.20
Sunflower	0.24	0.90	0.46	1.10	1.99
Cottonseed	0.05	0.49	0.89	0.75	3.64
Canola	0.04	0.74	1.59	0.70	3.57

[a]Calculated as oleic acid.
[b]V, W, X and Y are Gardner-Holdt viscosities; gel does not flow under prescribed conditions.

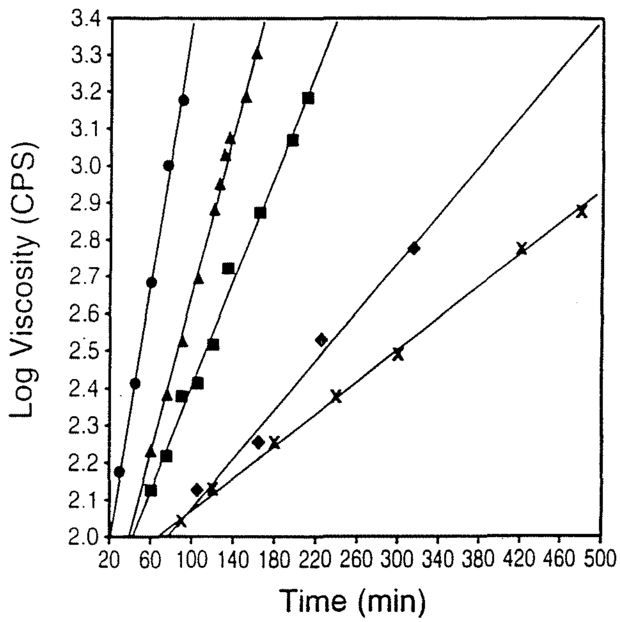

FIG. 1. Polymerization of vegetable oils at 330 ± 3°C. ●, sunflower oil; ▲, soybean oil; ■, safflower oil, ◆, cottonseed oil; x, canola oil.

A triglyceride molecule, consisting of three fatty acids at which addition may occur, introduces the possibility of forming complex structures and large molecules. Thus, the reaction time necessary to reach a desired viscosity depends on mass, structure of the reactants, rate of heat transfer and agitation. Gelling times at 330 ± 3°C for safflower (IV = 143.1), soybean (IV = 127.7), sunflower (IV

TABLE 3

Polymerization Rate Constants of Vegetable Oils

Oil	$K \times 10^{-3}$ at $330 \pm 3°C$
Safflower	17.23
Soybean	11.02
Sunflower	7.07
Cottonseed	3.21
Canola	2.14

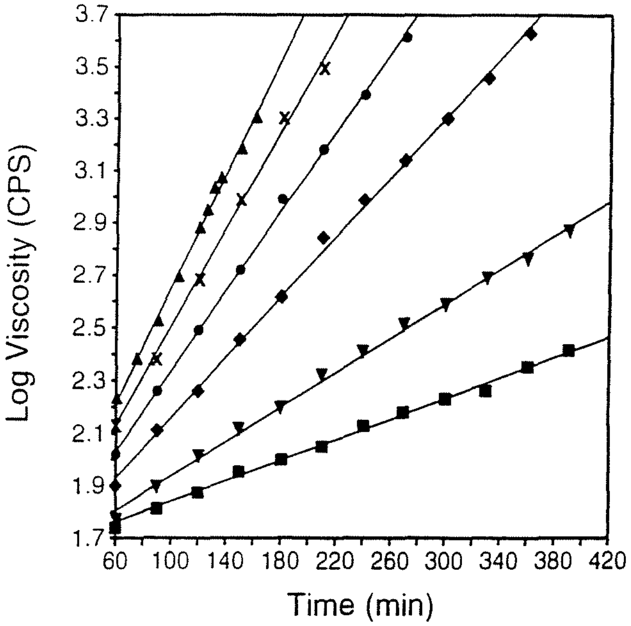

FIG. 2. Polymerization of soybean oil at different temperatures: ▲, 330°C; x, 320°C; ●, 310°C; ◆, 300°C; =▲, 290°C; ■, 280°C.

TABLE 4

Polymerization Rate Constants of Soybean Oil at Different Temperatures

Temperature $\pm$ 3°C	$K \times 10^{-3}$
330	11.02
320	9.44
310	7.61
300	5.73
290	3.27
280	1.99

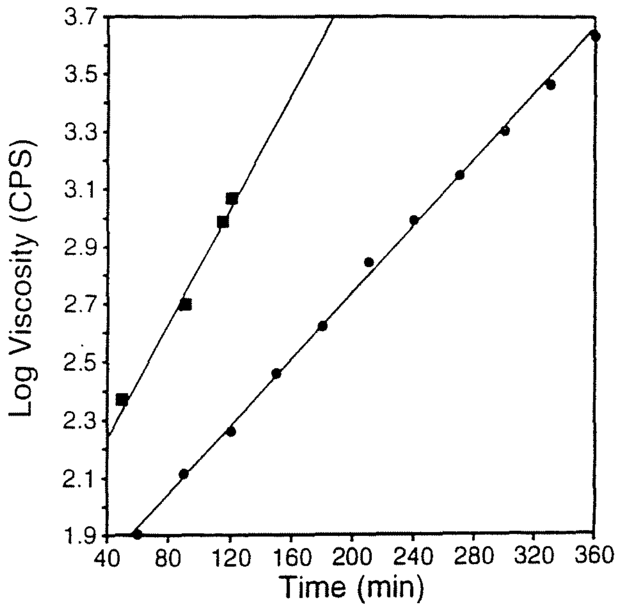

FIG. 3. Rate of polymerization of soybean oil with (■) and without (●) catalyst at 300 ± 3°C.

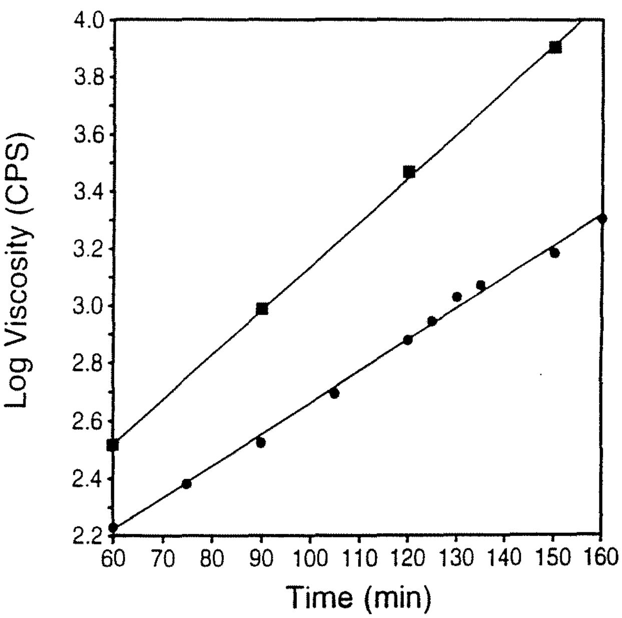

FIG. 4. Rate of polymerization of soybean oil with (■) and without (●) catalyst at 330 ± 3°C.

= 133.4), cottonseed (IV = 112.9) and canola (IV = 110.2) oils were 110, 255, 265, 390 and 540 min, respectively. Although IVs of cottonseed and canola oils are similar, canola oil, with its high oleic acid content, requires a longer time to gel.

Vehicles can be prepared by heat-bodying to specific characteristics or by blending various materials to provide appropriate properties. For example, heat-bodied oils of different viscosities can be blended to produce a desired vehicle viscosity. Gels can also be blended with unmodified oils to give appropriate characteristics. The principal advantage of these gels is that they can be prepared and stored as a stock material for subsequent custom blending of vehicles over a broad viscosity range. The viscosities of vehicles prepared by blending different proportions of the gel and unmodified oil can be seen in Table 5.

Apparent Mw values for selected, representative modified vegetable oil are given later in Tables 6–8. The Mw values are shown as apparent Mw for several reasons. Polystyrene (PS) was used as a standard for the molecular weights without correcting for the difference in "S" value between PS and the bodied oils. PS is a linear polymer,

TABLE 5

Gel-Oil Blends[a]

Composition (% w/w)		Vehicle
Gel	Oil	viscosity[b]
21.5–22.5	78.5–77.5	M–N
43.0–45.0	57.0–55.0	V
45.0–47.0	55.0–53.0	W
47.0–50.0	53.0–50.0	W–X
51.0–53.0	49.0–47.0	X–Y

[a]Gel-oil blends were prepared separately with soybean, sunflower, safflower, cottonseed and canola oil.
[b]Gardner-Holdt Viscosity Scale.

TABLE 6

Molecular Weights of Soybean Oil Vehicles

Vehicle viscosity[a]	Apparent[b] molecular weight
G–H	2656
M–N	3757
T–U	4991
U–V	5133
V	6030
W	6193
X–X	7208
X–Y	8851

[a]Gardner-Holdt Viscosity Scale.
[b]Obtained by GPC analysis.

TABLE 7

Vehicle Molecular Weight (Mw) and Viscosity

Oil used in vehicle	Vehicle viscosity[a]	Apparent[b] Mw
Canola oil	W	5928
	W–X	6656
	X–Y	8196
Cottonseed oil	W	5364
	W–X	7046
	X–Y	7644
Safflower oil	W	7191
	W–X	7215
	X–Y	7445
Sunflower oil	W	6165
	W–X	7345
	X–Y	8827

[a]Different viscosities were obtained by different heat-bodying times. Gardner-Holdt Viscosity Scale.
[b]Obtained by GPC analysis.

TABLE 8

Gel Molecular Weights (Mw)

Gel	Apparent Mw[a]
Soybean	60423
Canola	44924
Cottonseed	38266
Safflower	31772
Sunflower	15055

[a]Obtained by GPC analysis.

whereas bodied oils have varying degrees of branching. Thus, molecules of bodied oils of identical Mw's will have different radii of gyration and, therefore, appear at different elution volumes on GPC. As a consequence, only apparent MW's are attainable. The apparent Mw of relatively bulky unmodified soybean, sunflower, safflower, cottonseed and canola oils were obtained as 1428, 1148, 1357, 1151 and 1301, respectively, by this technique; however, the calculated molecular weights of these oils are ≈880.

Also, the GPC curves did not return to baseline at the low Mw end of the chromatograms due to minor amounts of low-molecular weight materials. These are omitted from the calculations; therefore, a degree of inaccuracy results. Weight average values are less influenced by the area lost than number averages; therefore, apparent Mw's are used in the tables.

Table 6 shows comparison values for Gardner-Holdt viscosities and apparent Mw of soybean oil vehicles. Table 7 summarizes vehicle Gardner-Holdt viscosities and corresponding apparent Mw for safflower, sunflower, cottonseed and canola-based vehicles. Viscosity increases are directly proportional to increases in apparent Mw and the degrees of polymerization. Differences of apparent Mw at the same viscosity of different oils may be due to differences in linearity of the bodied oils. Apparent Mw values of the vegetable oil-derived gels are given in Table 8. The differences among oils in apparent Mw at the gel point suggest a decrease in the size of the gel particles as one goes from soybean oil to sunflower oil.

Vehicles prepared by these technologies are compatible with pigments for producing the four colors commonly used in the newspaper printing industry—black, cyan, magenta and yellow. These vehicles are characterized by an exceedingly light coloration. Except for canola, they have values on the Gardner Color Scale of about six or less and typically are in the range of about 2–4 (13). This property permits some reduction in the amount of pigment required for colored inks as compared to the pigment levels required by the much darker commercial vehicles with Gardner Color values of about 14 and greater.

REFERENCES

1. Ono, T., K. Otake and K.T. Koko, Japanese Patent #123681 (1961).
2. Kuzuwata, M., and K.T. Koko, Japanese Patent #227287 (1963).
3. Gupta, P.K., J. Rai, and H. Singh, Indian Patent #154760 (1984).
4. Kobayaski, S., and K. Nozaki, Japanese Patent #17716 (1978).
5. Erhan, S.Z., and M.O. Bagby, U.S. Patent #5122188 (1992).
6. Moynihan, J.T., U.S. Patent #4419132 (1983).
7. Moynihan, J.T., U.S. Patent #4519841 (1985).
8. Moynihan, J.T., U.S. Patent #4554019 (1985).
9. *Manufacturing Directions for Soybean Oil-Based American Newspaper Publishers Association-INK*, American Newspaper Publishers Association, Reston, 1988.
10. *American Society for Testing and Materials, Book of ASTM Standards*, American Society for Testing and Materials, Philadelphia, 1963, pp. 66–68, ASTM D-1545-63.
11. *Ibid.*, 1980, pp. 264–265, ASTM D-1544-63.
12. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, edited by R.O. Walker, American Oil Chemists' Society, Champaign, 1990.
13. Erhan, S.Z., and M.O. Bagby, *J. Am. Oil Chem. Soc. 68*:635 (1991).
14. Erhan, S.Z., and M.O. Bagby, *J. Appl. Sci.*:1859 (1992).

[Received March 15, 1994; accepted June 21, 1994]